

Synthesis and Characterization of Copper Indium Sulfide Microsphere and its Application in Low-Cost Solar Cell

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CuInS₂ microsphere was synthesized by Ultrasonic method in propylene glycol, as solvent, and copper complex, indium chloride and thioacetamide (TAA) as precursors. Optimum conditions such as reaction time, solvent type, sulfur source, and ultrasonic power were determined. Then thin film of CuInS₂ was prepared and its application in solar cells was investigated. To investigate solar cell application of CuInS₂ in the present experiment, at first CuInS₂ paste was prepared from nanoparticle and then thin film prepared by doctor blading. I–V curves offer key parameters including short-circuit current (I_{sc}) and the open-circuit voltage (V_{oc}). Another important parameter for solar cells is fill factor (FF). A series of analysis including X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) spectroscopy were performed to characterize the CuInS₂ microsphere. The optical band gap of CuInS₂ microsphere was estimated to be 2.28 eV.

Keywords: Copper Indium Sulfide, Solar Cell, Sulfur Source, Fill Factor, Ultrasound Irradiation.

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1. INTRODUCTION

Copper indium sulfide is one of the chalcopyrite compounds used as absorber in thin film solar cells. Its properties and applications in technology are growing in comparison with those of materials which are widely researched such as Cu(In,Ga)Se₂ (CIGSe) compounds [1]. The I–III–VI₂ ternary semiconductors are now subject to substantial and extensive research interest since their band gap lies between 0.8 and 2.0 eV. As a result, they are classified as visible-light responsive photo catalysts. Also, these materials are considered as quality visible-light absorbers in the CIS solar cell [2, 3]. These special conditions of high temperature, pressure, and local intense micro mixing attained during acoustic cavitations lead to many unique properties in them irradiated solution and particles suspended in the same [4]. In this paper, CuInS₂ nanostructures were successfully prepared from the reaction of copper oxalate, InCl₃ and sulfide source by sonochemical method. In addition, effects of different sulfide sources on size and morphology of products were examined. Fabricated CuInS₂ was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. SYNTHESIS AND CHARACTERIZATION

2.1 Method of Sample Manufacturing and Analysis

At the first stage, CuInS₂ nanoparticles were prepared by the reaction of copper complex with indium chloride and thioacetamide in PG as solvent. The reaction was performed under ultrasound power. In a typical preparation, 0.305 mg of copper complex was dissolved in 20 ml of PG and was irradiated with high-intensity ultrasound. A solution consisting 20 mg of InCl₃ in 20 ml of PG was added drop-wise to the copper complex solution (mixture A). A solution of 5.2 mg SDS

in 20 ml of PG was added drop-wise to the mixture A. Then, a solution of TAA (135 mg) in 20 ml of PG was added drop-wise to the previous mixture during 30 minutes. The resulting black powder was filtered and washed three times with ethanol and distilled water. The washed powder was dried at 60 °C for 3 hours in vacuum. Dried precipitates were being annealed in Ar atmosphere at 350 °C for 2 hours. The annealing was the key parameters which were changed In₂S₃ and CuS to CuInS₂. A series of analysis including X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) spectroscopy were performed to characterize the CuInS₂ microsphere. The optical band gap of CuInS₂ microsphere was estimated to be 2.28 eV.

For preparing the CuInS₂ electrodes, the FTO glass used as recent collector (Solar 4mm thickness, Pilkington, tec 7, Japan) was primarily cleaned in a detergent solution using an ultrasonic bath for 10 minutes. Later, it was rinsed with water and ethanol, and then the CIS electrode was prepared by doctor blading of CuInS₂ paste on FTO (Solar 4 mm thickness, Pilkington, tec 7, Japan). The as-prepared electrodes were sintered at 350 °C for 30 minutes. CdS QDs were also deposited on the CuInS₂ film by the traditional CBD method.

3. RESULTS AND DISCUSSION

The as-synthesized products were characterized by powder X-ray diffraction (XRD). All the diffraction peaks from the XRD pattern of Fig. 1a matched with the standard JCPDS NO. 38-0777 pattern of tetragonal CuInS₂. Photoluminescence (PL) measurement of CuInS₂ nanosheet was carried out at room temperature with excitation wavelength of 344 nm that is shown in Fig. 1 b. The PL spectrum consists of one strong peak at 541.5 nm that can be ascribed to a high level transition in CuInS₂ semiconductor crystallites. It has been reported that this kind of band edge luminescence arises

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es from the recombination of shallowly and/or excitons trapped electron-hole pairs. By band gap calculation by using $E = 1240/\lambda_{\text{max}}$, band gap of as-synthesized sample was obtained as 2.21 eV, which shows blue shift compared with CuInS₂ bulk (1.52 eV).

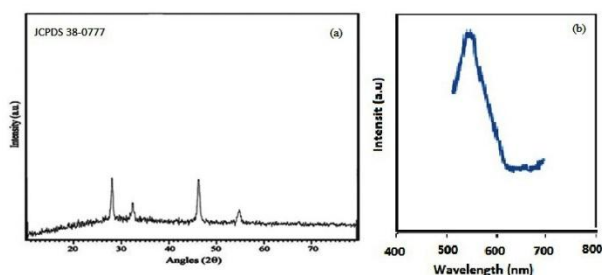


Fig. 1 – Patterns of prepared CuInS₂ sample 1, (b) Photoluminescence spectra of CuInS₂ disperse in ethanol at room temperature.

To investigate the effect of sulfide source on the morphology of the products, syntheses of CuInS₂ have been carried out by different sulfide sources. SEM observations of the CuInS₂ nanostructure with different sulfide source are shown in Fig. 2. When TSC was used as the sulfide source, sulfur can be released immediately, so CuS and In₂S₃ were formed quickly, and rate of nucleation was greater than growth. Sizes of particles were small, but these particles were agglomerated. Fig. 2a shows that by substituting the sulfide source with N₂H₄CS (TU), the sulfur can be released more slowly, but rate of creating nucleus was more than growth again. Small particles composed of microsphere obtained which were fused to each other. When TAA was used as the sulfur source, release rate of sulfur decreased in comparison with the prior state, so rate of growth was greater. In the meanwhile, larger particles were obtained in comparison with those sulfide sources mentioned previously but these particles were separated and microsphere with small particles was achieved again. With changing sulfur source to L-cyst, rate of nucleation and growth became optimum and the particles with uniform size of about 40 nm were obtained. Fig. 2b shows SEM of CuInS₂ when Na₂S₂O₃ was used as the sulfur source. Under such circumstances, small agglomerated particles were obtained. When TGA was used as the sulfur source and the rate of growth was greater than rate of nucleation and the particles became larger. Finally, when CS₂ was employed as the sulfur source, no products were obtained because CS₂ released sulfur very slowly.

To investigate solar cell application of CuInS₂ in the present experiment, at first CuInS₂ paste was prepared from nanoparticle and then thin film prepared by doctor balding. I–V curves offer key parameters including short-circuit current (ISC) and the open-circuit voltage (VOC). Another important parameter for solar cells is fill factor (FF). The SEM micrograph of CuInS₂ electrode made of CuInS₂ NPs show a rough surface layer containing large CuInS₂ chunks in which entity CuInS₂ particles are scarcely visible. The chunk structure is maybe formed through aggregation of CuInS₂ arranged in a side-by-side configuration. Another possible reason for appearance of irregular chunks on CuInS₂ layer is

the stress-induced surface rumpling caused by the fast cooling after annealing. Also, table 1 depicts the association between thickness and performance parameters. J_{sc} increased from 2.5(d1) to 14 μm(d2) but decreased with further increase in thickness. CdS in the film will build up with increasing thickness, and an increased J_{sc} would be expected. The charge recombination between electrons injected from the excited CdS to the conduction band of CuInS₂ and the I³⁻ ions in the electrolyte will, however, become more serious in thicker films, which is detrimental to electron collection on the back contact, and hence, photocurrent generation.

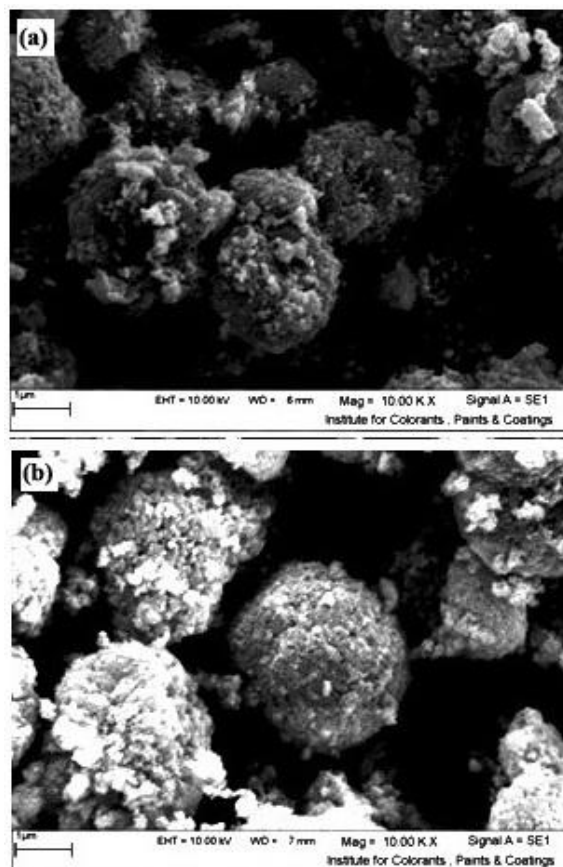


Fig. 2 – Effect of sulfide source on the morphology of products: a) TU, e) Na₂S₂O₃.

One can see from the trend of J_{sc} that CdS buildup dominates the photocurrent generation below 14 μm, resulting in an increase in J_{sc} until 14 μm. On the contrary, charge recombination plays a key role in the performance when the thickness is more than 14 μm. Contrary to the propensity of J_{sc}, V_{oc} decreased linearly with increasing film thickness. Charge recombination and mass transport limitations in the thicker film lead to a decreased V_{oc}. In addition, the series resistances of the thicker films grow quickly because the electrons and redox species migrate in a long path-length to complete the circuit. Balanced from V_{oc} and J_{sc} increased with thickness until 14 μm followed by a decrease. The result showed that the optimal thickness falls in the range of 12–16 μm. The CuInS₂ films present in this article had a thickness in the optimal range.

Table. 1 – Show depicts the correlation between thickness and performance parameters.

Thickness	$J_{sc}(\text{mA}\cdot\text{cm}^{-2})$	$V_{oc}(\text{mV})$	FF	η (%)
d1	1.34	680	0.539	0.49
d2	2.06	710	0.55	0.81
d3	1.24	680	0.538	0.45

CONCLUSIONS

The use of ultrasound irradiation in the synthesis of copper indium sulfide microsphere by copper oxalate, indium colored and thioacetamide have a marked effect

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on the morphology of the produced particles. The effect of some parameters such as solvent, sulfur source, power, and time duration of sonication on the morphology and size of the obtained products was investigated. This method proposes a broad idea to synthesize other rare-earth compounds with various morphologies and novel properties. The XRD, SEM, PL, and FTIR were used to characterize the products and the PL properties of CuInS_2 microsphere were discussed, and it applied in solar cell.

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